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(71) Applicant(s)
Denso Corporation

(Incorporated in Japan)

1-1 Showa-cho, Kariya-city, Aichi-pref 448, Japan

(72) Inventor(s)
Arimitsu Usuki
Makoto Kato
Akane Okada
Fumio Kato
Isamu Inai

(74) Agent and/or Address for Service
Withers & Rogers
4 Dyer's Buildings, Holborn, LONDON, EC1N 2JT, United Kingdom

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EP 0747322 A1 EP 0681990 A1 US 4889885 A

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(54) Clay composite material

(57) A clay composite material comprises an organic clay mineral prepared by ionic bonding of organic onium ions 6 having unsaturated carbon chains of at least 6 carbon atoms, guest molecules with polar groups in the molecules and with an unsaturated carbon chain whose molecular length is the same as or larger than that of the organic onium ions, and a crosslinking agent capable of forming crosslinked bonds between the unsaturated bonds of the organic onium ions and the unsaturated bonds of the guest molecules. The guest molecules are preferred to be oligomers or polymers of molecular weight 1000 to 100,000. The clay composite material is preferably kneaded in a rubber material.

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Fig.1(a)

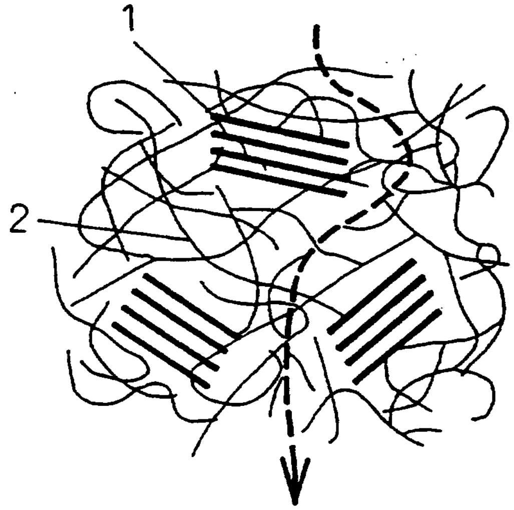


Fig.1(b)

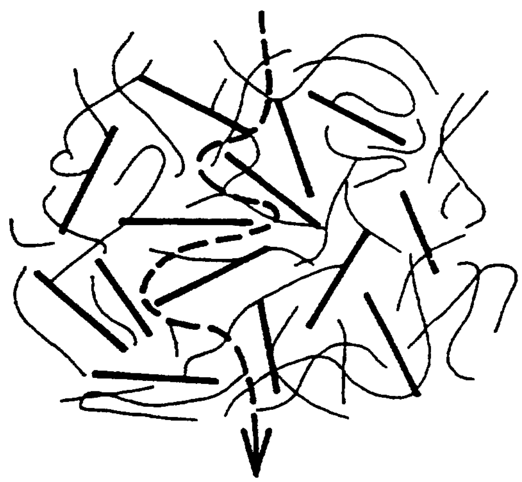
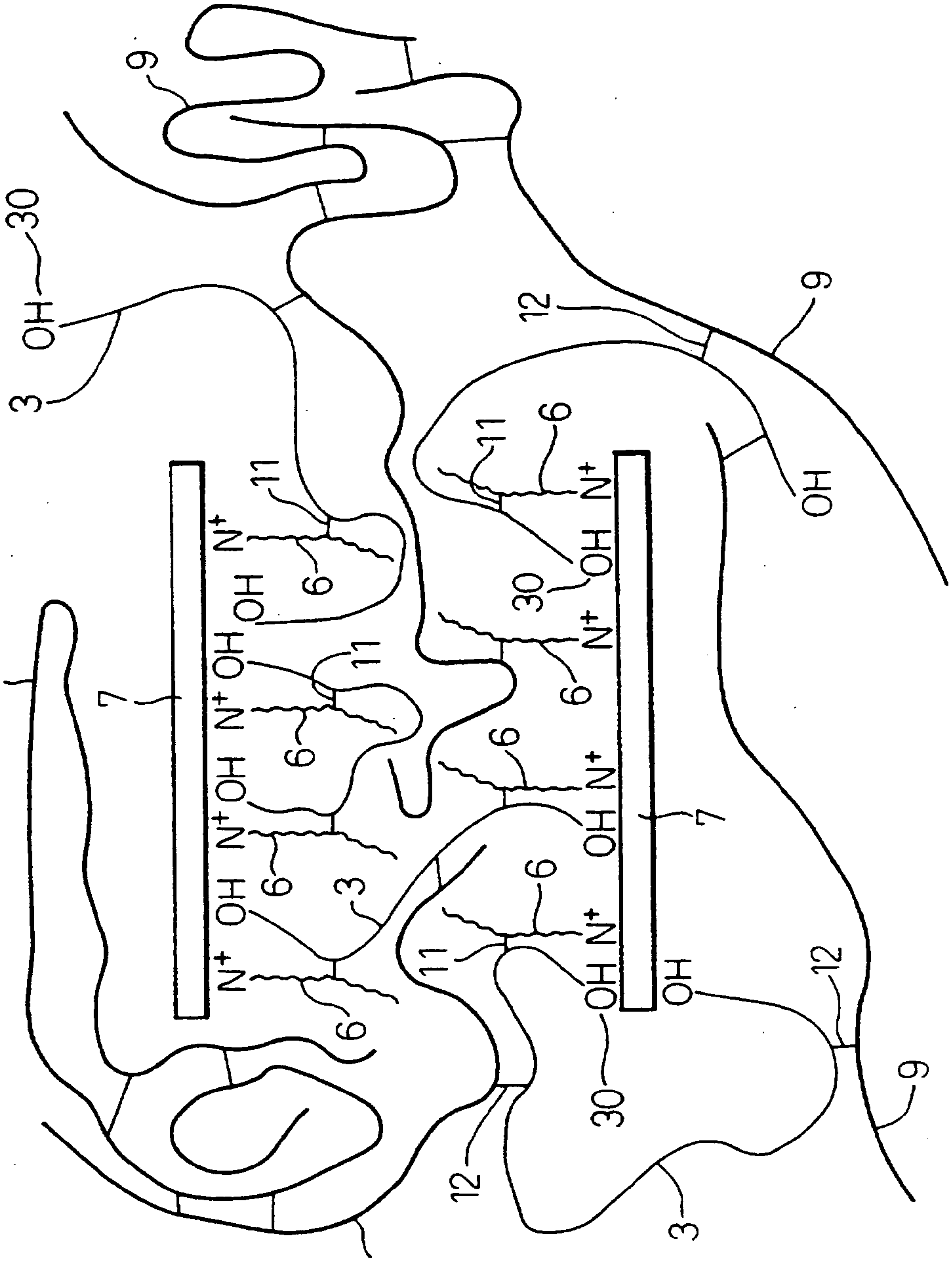


Fig.2



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CLAY COMPOSITE MATERIAL AND PROCESS FOR ITS PRODUCTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a clay composite material and a process for its production. More specifically, it provides a novel seed material which can disperse clay minerals in low polarity rubber at a molecular level.

2. Description of the Related Art

Additions and mixtures of clay minerals have been investigated for improving the mechanical characteristics of rubber materials. For example, in Japanese Unexamined Patent Publication No. 1-198645, there is disclosed a process whereby an organic clay mineral is prepared using an oligomer with onium ions introduced at the ends or side chains, and is combined with a rubber material.

However, the preparation of oligomers with onium ions introduced therein for such conventional clay composite rubber materials is not always simple. Furthermore, since the oligomer is introduced directly between the clay layers, swelling between the clay layers has often been insufficient.

According to Giannelis et al., when polystyrene containing no polar groups is used, only one layer of polystyrene molecules can be intercalated between the layers, and there is also a limit to interlayer swelling (E.P. Giannelis et al., Chem. Mater. 5, 1694-1696 (1993)).

The inventors of the present invention have already filed an application for a technique whereby an oligomer or polymer with polar groups in the molecule is fully incorporated between layers of a clay mineral made organic with onium ions, and a technique whereby an oligomer or polymer with no polar groups is introduced

between the layers of an organic clay mineral after introduction of a low molecular substance with polar groups. ("Clay Composite Material and Process for Its Production", filed June 5, 1995; "Clay Composite Material, Process for Its Production and Blend Material", filed June 30, 1995.)

However, mixture of guest molecules such as oligomers with rubber lowers the viscosity when unvulcanized and slightly lowers the elastic modulus even when vulcanized.

SUMMARY OF THE INVENTION

In light of these problems, it is an object of the present invention to provide a clay composite material which can evenly disperse clay minerals in polymers on a molecular level and has excellent mechanical strength and creep resistance, as well as a process for its production.

The present invention provides a clay composite material comprising a clay mineral; an organic onium ion having an unsaturated carbon chain of at least 6 carbon atoms ionically bonded to said clay mineral; a guest molecule having a polar group and an unsaturated carbon chain whose molecular length is the same as or larger than that of the organic onium ion; and a crosslinking bond between the unsaturated carbon chain of the organic onium ion and the unsaturated carbon chain of the guest molecule,

wherein at least a portion of the organic onium ion and the guest molecule is included between the layers of the clay mineral, and a hydrogen bond is formed between the clay mineral and the polar group of the guest molecule.

The present invention further provides a process for producing a clay composite material to be kneaded with a rubber material, comprising the steps of forming an ionic bond between a clay mineral and an organic onium ion having an unsaturated carbon chain of at least 6 carbon

atoms, to prepare an organic clay mineral;

contacting the organic clay mineral with a guest molecule having a polar group and having an unsaturated carbon chain whose molecular length is the same as or larger than that of the organic onium ion, so that at least a part of the guest molecule is included between the layers of the organic clay mineral and a hydrogen bond is formed between the organic clay mineral and the polar group of the guest molecule, and

mixing the organic onium ion and the guest molecule with a crosslinking agent to form a crosslinked bond between the unsaturated bond of the organic onium ion and the unsaturated bond of the guest molecule.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1(a) and Fig. 1(b) are schematic drawings illustrating the function and effect of the clay composite material according to the invention.

Fig. 2 is a schematic drawing illustrating the construction of an embodiment of the clay composite material according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The most notable features of the present invention are that the organic clay mineral is prepared by forming ionic bonds between the clay mineral and the organic onium ions with the unsaturated carbon chains, and that crosslinked bonds are formed between the organic onium ions and the guest molecules.

The function and effect of the present invention will now be explained.

The clay composite material of the invention is rendered organic by forming ionic bonds between the clay mineral and the organic onium ions. The organic clay mineral has a wide spatial area. Consequently, the guest molecules can easily be included between the clay mineral layers.

While non-polar molecules can be intercalated between clay mineral layers, these have usually been

eliminated by the polarity of the silicate layers.

According to the invention, however, guest molecules having polar groups added to non-polar molecules are intercalated between the clay mineral layers. Consequently, the guest molecules which have penetrated between the clay mineral layers form hydrogen bonds between its unsaturated groups and the silicate layers of the clay mineral. Therefore, even though the guest molecules have non-polar regions, they can remain between the layers due to the hydrogen bonds stably formed between their unsaturated groups and the clay mineral.

Thus, even non-polar molecules which have caused a difficulty due to the swelling of clay minerals can remain between clay mineral layers, by the introduction of at least one polar group into each of the guest molecules according to the invention. Consequently, swelling between the clay mineral layers can occur in an unlimited manner beyond the conventional limit for interlayer swelling.

The clay composite material according to the invention has higher barrier properties compared to the limited swelling of the prior art, because of the aforementioned unlimited swelling of the clay mineral.

This will now be explained with reference to Fig. 1(a) and Fig. 1(b).

According to the prior art, when a clay mineral 1 is added to rubber molecules 2 in a state which allows only limited swelling, as shown in Fig. 1(a), large gaps are produced between the clay mineral 1, resulting in a lower barrier property against gas and water. However, if the distance between the layers of the clay mineral 1 is increased it is possible to finely disperse the clay mineral 1 among the rubber molecules 2. As a result, the barrier property against gas and water may be increased, as shown in Fig. 1(b). The arrows in Fig. 1(a) and Fig. 1(b) indicate the route of water or gas, showing that this detoured penetration of the water or gas improves

the barrier property.

Also, the presence of the clay mineral restricts this behavior of the guest molecules. The intertwined guest molecule chains are therefore more resistant to loosening. This results in increased mechanical strength, including tensile strength and elastic modulus of the material. The creep resistance is also improved.

Ammonium salts of alkylamines are often used as organic onium ions to prepare organic clay minerals, but alkylamines have no unsaturated bonds and therefore no site for reaction with the oligomer. Consequently, alkylamines have only been used as plasticizers in rubber.

According to the invention, guest molecules with unsaturated carbon chains are used as the guest molecules, and organic onium ions with unsaturated carbon chains are used as the organic onium ions. A crosslinking agent which can bond together the unsaturated bonds of the guest molecules is also added to the clay composite material. Crosslinked bonds are therefore formed between the unsaturated bonds of the guest molecules and the unsaturated bonds of the organic onium ions. This crosslinked bonding restricts movement of the rubber molecules adjacent to the silicate layers of the clay mineral, thus advantageously affecting the dynamic properties of the clay composite rubber material.

The clay composite material of the invention will now be explained in more detail.

The clay composite material comprises a clay mineral, an organic onium ion as the organic part of the clay mineral, guest molecules enclosed between the clay mineral layers, and a crosslinking agent which forms crosslinked bonds between the organic onium ions and the guest molecules.

The clay mineral used is preferably one which has a large contact area with the guest molecules. This allows greater swelling between the clay mineral layers.

Specifically, the cation exchange capacity of the clay mineral is preferably 50-200 milliequivalents/100 g. If it is less than 50 milliequivalents/100 g, the onium ion exchange becomes insufficient, often impeding swelling between the clay mineral layers. Conversely, if it is greater than 200 milliequivalents/100 g, the bonding force between the clay mineral layers becomes too strong, which also can impede swelling between the layers.

The clay mineral may be a smectite-based clay mineral such as montmorillonite, saponite, hectolite, beidellite, stevensite, nontronite, etc. or vermiculite, halloysite, swellable mica, etc., and may be either natural or synthesized.

The organic onium ion has an unsaturated carbon chain of at least 6 carbon atoms. With less than 6 carbon atoms, the hydrophilicity of the organic onium ion is increased, lowering its compatibility with the guest molecule. The organic onium ion may be, for example, an ammonium salt of an alkenylamine. Examples of alkenylamines include 1-hexenylamine, 1-dodecenylamine, 9-octadecenylamine (oleylamine), 9,12-octadecadienylamine (linolamine), 9,12,15-octadecatrienylamine (linoleylamine), etc.

The guest molecules have polar groups in the molecules. A polar group is one which has a localized electron in the guest molecule, producing an unbalanced charge, but without a fully polarized ion. Thus, onium ions are not included in the polar groups.

The guest molecules may have one or more polar groups selected from the group consisting of hydroxyl (OH), halogens (F, Cl, Br, I), carboxyl (COOH), anhydrous carboxyl (-COO-CO-), thiol (SH), epoxy and amino (NH_2).

The guest molecules have a molecular length which is the same as or larger than that of the organic onium ions. When the molecular length of the guest molecules is smaller than the molecular length of the organic onium

ions, the guest molecules may not protrude outward from the region where the organic onium ions are present at the interface with the clay mineral. Consequently, the clay mineral sometimes fails to easily disperse in the matrix of the rubber material, etc.

The guest molecules have unsaturated carbon chains with unsaturated bonds in the molecules. The unsaturated bonds are highly reactive, forming crosslinked bonds with the unsaturated bonds of the organic onium ions in the presence of a crosslinking agent.

The guest molecules are preferably oligomers or polymers of molecular weight 1000-100,000. If the molecular weight is under 1000, swelling between the clay mineral layers can be insufficient. If the molecular weight exceeds 100,000, the guest molecule becomes less soluble in the solvent, and the softening point or melting point may become higher than the decomposition point of the clay mineral.

At least a portion of the guest molecules are included between the clay mineral layers. It is not necessary for the all of the guest molecules to be included between the clay mineral layers. For example, sufficient swelling between the layers is achieved if at least 10 wt% of the total weight of the guest molecules is included. At less than 10 wt%, the swelling between the clay mineral layers may be insufficient.

The crosslinking agent forms crosslinked bonds between the unsaturated bonds of the organic onium ions and the unsaturated bonds of the guest molecules. The crosslinking agent may be any one which is used for crosslinking of rubber, and especially it is preferred to comprise one or more types selected from the group consisting of sulfur, peroxides and phenolic resins. The reason is that the above-mentioned crosslinking agents are most suitable as rubber crosslinking agents, and may therefore form the above-mentioned crosslinked bonds most efficiently.

The clay composite material is preferably kneaded into the rubber material. This allows even dispersion of the clay mineral at a large interlayer distance, even in rubber materials which have conventionally presented difficulty for dispersion of clay minerals. The unsaturated groups of the guest molecules are vulcanized with the rubber. Thus, crosslinked bonds are formed in a 3-component system consisting of the guest molecules, the rubber and the organic onium ions, to provide a clay composite rubber material with more excellent characteristics.

The rubber material may be, for example, either the same or a different species than the guest molecules. Such rubber materials include, but are not limited to, butyl rubber, butadiene rubber, ethylene-propylene-diene rubber, natural rubber and polyisoprene.

When the rubber material is a different species than the guest molecules, the interlayer distance of the clay mineral is preferred to be even wider. This allows an even dispersion of the clay mineral in the rubber material.

The present invention also provides a process for producing a clay composite material for kneading with a rubber material. The most notable features of this production process are that the organic onium ions which are the organic agent for the clay mineral have unsaturated carbon chains, the guest molecules which are included between the clay mineral layers have unsaturated carbon chains, and crosslinked bonds are formed between the unsaturated carbon chains in the organic onium ions and the unsaturated carbon chains in the guest molecules.

The function and effect of the process for producing the clay composite material will now be explained.

In this production process, the organic onium ions are ionically bonded with the clay mineral to prepare an organic clay mineral. This generates adequate space for the guest molecules to be included between the clay

mineral layers.

Thus, when the guest molecules are contacted with the organic clay mineral, the guest molecules are easily included in the spaces between the layers. Since the guest molecules have polar groups, they form hydrogen bonds with the clay mineral and remain between the clay mineral layers, while the area between the clay mineral layers is hydrophobic. Therefore, the low polarity guest molecules included between the clay mineral layers are stably retained between the layers without being eliminated by the polarity of the clay mineral.

The guest molecules are bulky, having a molecular length which is the same as or greater than that of the organic onium ions. Hence, retention of the guest molecules between the layers creates a state allowing indefinite swelling in which there is no limit to the swelling between the layers.

Consequently, kneading of this indefinitely swellable clay composite material in a rubber material allows even dispersion of the originally polar clay mineral in the low polarity rubber material, on a molecular level.

Since the clay mineral is in a state which allows indefinite swelling as mentioned above, the surface area is increased, providing a high barrier property against gas and liquids (water, oils, etc.). The presence of the guest molecules in the clay mineral also provides a restriction to movement. The intertwined guest molecule chains are therefore more resistant to loosening. This results in increased mechanical strength, including tensile strength and elastic modulus of the material. The creep resistance is also improved.

The guest molecules have unsaturated carbon chains, while the organic onium ions also have unsaturated carbon chains. Consequently, when the organic onium ions and the guest molecules are kneaded in a rubber material, crosslinked bonds are formed in a 3-component system of

the rubber, the organic onium ions and the guest molecules in the presence of a crosslinking agent.

Thus, the dynamic characteristics of the rubber material may be improved since the clay mineral is in a state allowing indefinite swelling and a 3-component system of crosslinked bonds is formed in the rubber.

The process for producing the clay composite material will now be explained in more detail.

The method of contacting the clay mineral with the organic onium ion may be, for example, an ion-exchange method. The ion-exchange method may be one wherein, for example, the clay mineral is immersed in an aqueous solution containing the organic onium ion, and then the clay mineral is washed with water to remove the excess organic onium ion.

The method of contacting the guest molecules with the organic clay mineral may be, for example, (1) a method wherein the guest molecules are swelled in a solvent and the clay mineral is contacted with the guest molecules in that swelled state, after which the excess solvent is removed, or (2) a method wherein the clay mineral is contacted with the guest molecule component which has been softened or melted by heat.

According to method (1) above, the guest molecules may be included between the clay mineral layers at room temperature. Solvents which may be used for this method include non-polar solvents such as toluene, benzene, xylene, hexane and octane.

According to method (2) above, the guest molecule component is softened or melted by heating the guest molecule to the same or a higher temperature than the softening or melting temperature. The heating is carried out at a temperature at which the guest molecule and clay mineral are stable without decomposing. For example, the heating temperature is preferred to be no higher than 250°C. If it exceeds 250°C, the organic clay mineral may decompose.

The other aspects of the process for producing the clay composite material are the same as explained for the clay composite material itself.

Examples of the present invention will now be provided, with the understanding that the invention is in no way limited to these examples.

Example 1

A clay composite material according to this example of the invention will be explained with reference to Fig. 2.

As shown in Fig. 2, this clay composite material is prepared by kneading a clay mineral 7 which has been made organic with organic onium ions 6, and guest molecules 3 with unsaturated carbon chains having polar groups 30 in the molecules, in the presence of a crosslinking agent.

Some of the organic onium ions 6 and the guest molecules 3 are included between the layers of the clay mineral 7.

The clay mineral 7 is sodium-type montmorillonite (ion-exchange capacity: 120 meq/100 g, Yamagata Prefecture). The organic onium ions 6 are oleylammonium ions with a carbon number of 18, and they have one double bond in each molecule. The guest molecules 3 are polyisoprene (LIR506, product of Kuraray) with hydroxyl groups, having a molecular weight of about 25,000. The guest molecules 3 are as large as or larger than the molecular length of the organic onium ions 6. Sulfur is used as the crosslinking agent.

The process for producing the clay composite material will now be explained.

First, 20.0 g of montmorillonite was dispersed in 2000 ml of water at 80°C. Then, 8.8 g of oleylamine hydrochloride was dissolved in 1500 ml of water at 80°C. The two aqueous solutions were mixed at once, and a precipitate was produced. The precipitate was washed twice with water at 80°C, to obtain montmorillonite rendered organic, i.e. ion-exchanged, with the

oleylammonium ion. This was called OL-montmorillonite. The inorganic content of the OL-montmorillonite as determined by the cauterization residue method was 69.4 wt%. Upon measurement of the distance between the montmorillonite layers by X-ray diffraction, the distance between the OL-montmorillonite layers was found to be 22.5 Å.

Next, 100 g of LIR506 was added to 100 g of OL-montmorillonite and mixed therewith at 80°C for 4 hours. The distance between the montmorillonite layers in the clay composite material as measured by X-ray diffraction was 70.0 Å.

To this mixture there were then added 3.0 g of sulfur (crosslinking agent), 5.0 g of zinc oxide, 3.0 g of stearic acid and 1.5 g of a vulcanizing accelerator (Noxela-MSA-G, product of Ouchi Shinko Kagaku Kogyo, KK.), and kneading resulted in a clay composite material as a seed material for natural rubber.

The seed material was added to natural rubber and kneaded to obtain a clay composite rubber material.

The function and effect of this example will now be explained.

As shown in Fig. 2, the clay composite material of this example has an even dispersion of the clay mineral 7 in the rubber molecules 9 since the organic onium ions 6 and guest molecules 3 are included between the layers of the clay mineral 7. Also, crosslinked bonds 11 are formed between the unsaturated bonds of the guest molecules 3 and the unsaturated bonds of the organic onium ions 6 in the seed material. Crosslinked bonds 12 are also formed between the unsaturated bonds of the guest molecules 3 and the rubber molecules 9.

The movement of the rubber molecules near the silicate layer of the clay mineral is thus restricted, for a favorable effect on the dynamic properties of the clay composite rubber material.

Example 2

The clay composite material of this example differs from that of Example 1 in that a 1,2-polybutadiene oligomer was used as the guest molecule.

The clay composite material of this example was prepared by mixing 100 g each of OL-montmorillonite and the 1,2-polybutadiene oligomer (G3000, product of Nihon Soda). The distance between the layers of the OL-montmorillonite (organic clay mineral) was 67.0 Å.

To this mixture there were then added 3.0 g of sulfur (crosslinking agent), 5.0 g of zinc oxide, 3.0 g of stearic acid and 1.5 g of a vulcanizing accelerator (Noxela-TTP, product of Ouchi Shinko Kagaku Kogyo, KK.), and kneading resulted in a clay composite material as a seed material for butadiene rubber.

The seed material was added to butadiene rubber and kneaded to obtain a clay composite rubber material.

The clay composite material of this example provided the same effect as Example 1.

Example 3

The clay composite material of this example differs from that of Example 1 in that 1-dodecenylamine was used as the organic onium ion.

The clay composite material of this example was prepared using 6.4 g of 1-dodecenylamine hydrochloride instead of the oleylamine hydrochloride in Example 1, to obtain the organic montmorillonite. The organic montmorillonite was called DO-montmorillonite.

Next, 100 g each of DO-montmorillonite and a hydrogenated 1,4-polybutadiene oligomer (Polytale H, product of Mitsubishi Chemicals) were mixed. The distance between the layers of the DO-montmorillonite (organic clay mineral) was 67.0 Å.

To the clay composite material there were then added 3.0 g of sulfur (crosslinking agent), 5.0 g of zinc oxide, 3.0 g of stearic acid and 1.5 g of a vulcanizing accelerator (Noxela-MSA-G, product of Ouchi Shinko Kagaku Kogyo, KK.), and kneading resulted in a seed material for

butyl rubber (clay composite material).

The seed material for butyl rubber was kneaded with a rubber material to obtain a clay composite rubber material.

The clay composite material of this example provided the same effect as Example 1.

According to the present invention it is possible to evenly disperse clay minerals in polymers on a molecular level, and thus to provide clay composite materials with excellent mechanical strength and creep resistance, as well as a process for their production.

CLAIMS

1. A clay composite material comprising a clay mineral; an organic onium ion having an unsaturated carbon chain of at least 6 carbon atoms ionically bonded to said clay mineral; a guest molecule having a polar group and an unsaturated carbon chain whose molecular length is the same as or larger than said organic onium ion; and a crosslinking bond between the unsaturated carbon chain of said organic onium ion and the unsaturated carbon chain of said guest molecule,

wherein at least a part of said organic onium ion and said guest molecule is included between the layers of said clay mineral, and a hydrogen bond is formed between said clay mineral and the polar group of said guest molecule.

2. A clay composite material according to claim 1, wherein the polar group of said guest molecule is at least one selected from the group consisting of hydroxyl (OH), halogens (F, Cl, Br, I), carboxyl (COOH), anhydrous carboxyl (-COO-CO-), thiol (SH), epoxy and amino (NH_2).

3. A clay composite material according to claim 1, wherein said guest molecule is an oligomer or a polymer of molecular weight 1000 to 100,000.

4. A clay composite material according to claim 1, wherein said crosslinking bond is at least one bond selected from the group consisting of a sulfur bond, an oxygen bond and a phenylene oxide bond.

5. A process for producing a clay composite material to be kneaded with a rubber material, comprising the steps of forming an ionic bond between a clay mineral and an organic onium ion having an unsaturated carbon chain of at least 6 carbon atoms, to prepare an organic clay mineral;

contacting said organic clay mineral with a guest molecule having a polar group and having an unsaturated carbon chain whose molecular length is the

same as or larger than said organic onium ion, to include at least a portion of said guest molecule between the layers of said organic clay mineral and form a hydrogen bond between said organic clay mineral and the polar group of said guest molecule; and

mixing said organic onium ion and said guest molecule with a crosslinking agent to form a crosslinked bond between the unsaturated bond of said organic onium ion and the unsaturated bond of said guest molecule.

6. A process for producing a clay composite material according to claim 5, wherein said crosslinking agent comprises one or more types selected from the group consisting of sulfur, peroxides and phenolic resins.

7. A clay composite material substantially as described herein with reference to the accompanying drawings.

8. A process for producing a clay composite material, the process being substantially as described herein with reference to the accompanying drawings.

The Patent Office

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Application No:	GB 9712928.2	**Examiner:**	Miss M. M. Kelman
Claims searched:	1 to 8	**Date of search:**	5 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C1A APC, C3K KGF KGG

Int Cl (Ed.6): C01B 33/00, 33/20, 33/38, 33/44; C08K 9/00, 9/04

Other: ONLINE: CHABS, CLAIMS, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X,P	EP 0747322 A1	KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO see the claims, page 10, line 15, to page 12, line 20, and Example 19	1 to 8
X	EP 0681990 A1	RHEOX INTERNATIONAL see Examples 52,73 and 77	1,2,7,8
A	US 4889885 A	KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.